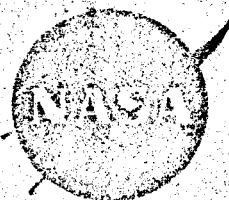


**IMPROVED SEPARATORS
FOR
SILVER OXIDE-ZINC
AND
SILVER OXIDE-CADMIUM CELLS
FOR SPACECRAFT APPLICATION**

by
HELMUTH L. PFLUGER
and
HOWARD E. HOYT



FIRST QUARTERLY REPORT

prepared for
GODDARD SPACE FLIGHT CENTER
CONTRACT NAS 5-9107
Modification 6

THE BORDEN CHEMICAL COMPANY

Central Research Laboratory
Philadelphia, Penna. 19124

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TABLE OF CONTENTS

	<u>Page No.</u>
INTRODUCTION	1
SUMMARY & CONCLUSIONS	2
DATA & DISCUSSION	4
A. Modification of Methyl Cellulose-	
Polyacid Films with Amines	4
Table I. - Comparison of Hydroxypropylamine with	
Potassium Hydroxide as Modifiers of B3.3 Film	5
Figure 1. - Effect of Base on Resistance of B3.3 Film	6
Figure 2. - Effect of Base on Flex of B3.3 Film	6
Figure 3. - Effect of Triethanolamine on Flex and	
Resistance of B2 Films	8
Figure 4. - Effect of Triethanolamine on Flex and	
Resistance of C2 Films	9
Table II. - Films Modified with Triethanolamine	10
Extractability of Amine	11
B. Modification of Methyl Cellulose Films with	
Salts of Organic Acids	12
Table III. - Modification of Methyl Cellulose with	
Potassium Salts of Organic Acids	13
Figure 5. - Dependence of Film Resistance	
Upon Equivalency	14
C. Modification of Methyl Cellulose By Pre-Swelling	
in 15% KOH	15
D. Modification of Methyl Cellulose and Methyl Cellulose/	
Polyacids with Glycols and Related Materials	16
Table IV. - Effect of Glycols and Related Additives	
on Properties of Methyl Cellulose	
Membranes	17
E. Effect of Elevated Temperatures on C3 Film	18
F. Effect of Radiation on C3 Film	19
Table V. - Effect of Irradiation on Tensile	
Properties of C3 Film	20
G. Gas Evolution in C3 Cells	21
H. Shorting of Cells on Standing	22

TABLE OF CONTENTS (CONTINUED)

	<u>Page No.</u>
J. Physical Modification of Polyethylene Films	23
Table VII. - Effect of Swelling in Solvent Followed by Extraction in 45% KOH Upon Resistance of Polyethylene-Type Films . . .	24
K. Polyvinyl Pyridine-Polyacid Co-acervate Films	25
Table VIII. - Properties of Polyvinyl Pyridine- Polyacid Co-acervate Films	26
ITEMS OF NEW TECHNOLOGY	27

PROJECT PERSONNEL

In carrying out the experimental work herein reported, the writers were assisted at The Borden Chemical Company by Dr. George Kitazawa, Head of the Physical Testing Laboratory; Mr. Richard Trickey, Chemist, and Mr. Ronald G. Burton, Assistant. At the Carl F. Norberg Research Center of the Electric Storage Battery Company, the subcontract tests are being supervised by Mr. J. Kelley.

INTRODUCTION

This is the First Quarterly Progress Report under NAS-5-9107, Modification 6, continuing the original contract NAS-5-9107 which was summarized in the Final Report (November 10, 1964 - November 10, 1965). The purpose of the current work is the further development of membranes suitable for use in alkaline cells such as secondary silver-zinc or silver-cadmium cells.

Earlier work resulted in materials whose use has extended cell-life five-fold and prevented catastrophic shorting due to zinc dendrite growth. The best performance was exhibited by membranes composed chiefly of methyl cellulose and modified by various chemical or physical means to improve electrolytic conductivity, dry flexibility and other pertinent properties. Several lines of approach to further improvements of modified methyl cellulose films seemed sufficiently promising to justify additional work in this area. Progress in modification of methyl cellulose is described in the present report.

Also reported herein are further investigations of the properties of previously developed membranes. These include the effects of radiation, of dry heat and of standing in a charged cell. The problem of frothing encountered with methyl cellulose/PVAA combinations is discussed briefly.

Work has continued on diffusion of silver through experimental membranes, using a radiotracer technique. The relationship of silver diffusion to membrane composition will be presented in the Second Quarterly Report.

Among new polymers of non-cellulosic structure, a co-acervate of vinyl pyridine and polyacrylic acid was prepared and is being tested. The possibility of physically modifying polyethylene films is being examined. Further exploration in the area of new synthetic membranes will be a topic of the Third Quarterly Report.

Promising membranes are being screened by the Norberg Research Center of the Electric Storage Battery Company, under sub-contract. Tests are carried out in simple cells under an accelerated regime. Results of these tests will be summarized in the Final Report.

SUMMARY AND CONCLUSIONS

Methyl cellulose-polyacid films may be prepared with extremely low resistances in 45% KOH by casting them from solutions buffered to pH in the range 3 to 6. At pH above 4 hydroxyamines like 3-hydroxypropylamine and triethanolamine are more effective than potassium hydroxide in that they act as flexibilizing agents for the dry film, making for superior facility in handling.

Addition of 10% triethanolamine to E2 Formulation (20% polyacrylic acid; 80% methyl cellulose) lowers resistance by 70%, increases flexibility by 350%. Addition of 10% triethanolamine to C2 Formulation (20% 1:1 copolymer of vinyl methyl ether and maleic anhydride; 80% maleic anhydride) lowers resistance by 83%, increases flexibility by 230%.

Both hydroxypropylamine and triethanolamine are completely soluble in 45% KOH and have been shown to be extractable under conditions of the resistance test. The extractability is believed to be a factor in the lowered resistance.

Studies of salt addition to methyl cellulose were extended to include salts of higher aliphatic acids and lower dibasic acids. Resistance lowering appeared to be related to the amount of acid function added, expressed as acid equivalents per equivalent of methyl cellulose monomer unit.

A methyl cellulose film, equilibrated first in 15% KOH, then in 30% KOH, gave a resistance of 17.3 milliohms-in.² on a 1.5 mil film as against 798 milliohms-in.² when equilibrated directly in 30% KOH. Accompanying the resistance lowering, a thirty-fold increase in the diffusion rate of silver occurred.

Glycols and related hydroxylated materials reduced resistance in methyl cellulose and methyl cellulose-polyacid films in some instances, but not as effectively as amines or organic acid salts.

Irradiation by Cobalt 60 of a cell prepared with C3 separator resulted in a 24% lowering of the wet tensile strength. NASA has reported that cellophane separators under the same conditions were welded together.

Gas evolution during charging of a cell constructed with C3 was demonstrated to be neither CO₂ nor oxygen and is presumed to be hydrogen. The accompanying frothing may be due to traces of cellulosic surfactant from the separator, but this explanation has not been confirmed.

A film prepared by co-acervation of poly 4-vinyl pyridine and polyacrylic acid showed low resistance in 30% KOH (9.9 milliohms-in.² and 1.5 mil film) and moderate resistance in 45% KOH (253 milliohms-in.²). The silver diffusion rates were comparable to those found for C3.

Polyethylene films were treated with KOH-extractable swelling agents to reduce electrolytic resistance. Although lowered by two to three orders of magnitude, the resulting resistances were too high to be of practical interest.

A charged silver-cadmium cell prepared with C3 separator shorted after three months stand time in tests at the Jet Propulsion Laboratory. Examination of the separator showed no apparent loss in strength or mechanical defects. However, silver was uniformly deposited in each of 5 wraps. The separator from a silver-zinc cell which had undergone 85 cycles, on the contrary, showed high silver content next to the electrode and almost none in the outer wrap. The relation of stand time failure to silver diffusion rate is under continued study.

A. Modification of Methyl Cellulose-Polyacid Films with Amines

The addition of organic amines to methyl cellulose-polyacid compositions was extensively explored during the third quarter of the previous contract. The observed improvement in conductivity could be attributable severally to salt formation with the polyacid, to enhancement of polarity by the amine group or to extraction of the bulky amine by the cell liquid filling a greater volume of film interstices with conductive solution. It was therefore of interest to compare an organic base with potassium hydroxide at levels roughly corresponding to equal degrees of salt formation or buffering. This was done by adding to the 10% aqueous solution of the polymers sufficient of each base to bring the solution to the same pH (within 0.1 unit). The polymer composition selected for the experiment was B3.3 (33% polyacrylic acid, 67% methyl cellulose) and the organic base was 3-hydroxypropylamine.

Data on electrolytic resistance of films swollen in 45% KOH are summarized in Table I. It appears that the organic base is more effective than KOH in lowering the resistance at equal degrees of salt formation initially in the dry film. However, the decrease in resistance is about the same on a weight percent basis regardless of whether the base is hydroxypropylamine or KOH, as is evident from the plot in Figure 1. These facts strongly suggest that on equilibration with electrolyte the amine may be replaced by a roughly equal weight of KOH. Evidence for the extractability of amine by electrolyte will be presented below.

TABLE I. - Comparison of Hydroxypropylamine With Potassium Hydroxide
as Modifiers of E3.3 Film

Reference	pH (a)	(b) Base Added		Film Properties		
		Percent KOH	Amine	Thickness (mils)	Resistance milliohms- cm ² (c)	MIT Flex (Cycles) (d)
421-113	2.8	0	0	1.5	315	(30a)
504-18	3.5	1.8	-	1.6	367	1229
504-16	4.0	3.4	-	1.6	200	1688
504-19	4.1	-	5.3	1.4	134	1682
504-15	4.4	5.3	-	1.4	97	1747
504-23	4.4	-	7.5	1.4	40	2757
509-17	5.1	10.8	-	1.7	47	232
504-24	5.0	-	14.4	1.6	14	4958
504-25	6.1	-	25.0	1.8	11	1311

(a) pH of a 10% aqueous solution of polymer mixture containing 33 parts by weight polyacrylic acid and 67 parts methyl cellulose, after addition of stated amount of base.

(b) Weight percent of polymer solids.

(c) Electrolytic resistance of film swollen in 45% KOH.

(d) ASTM Folding Endurance Test for Paper, D643-43; 200 g. tension on film conditioned at 50% R.H.

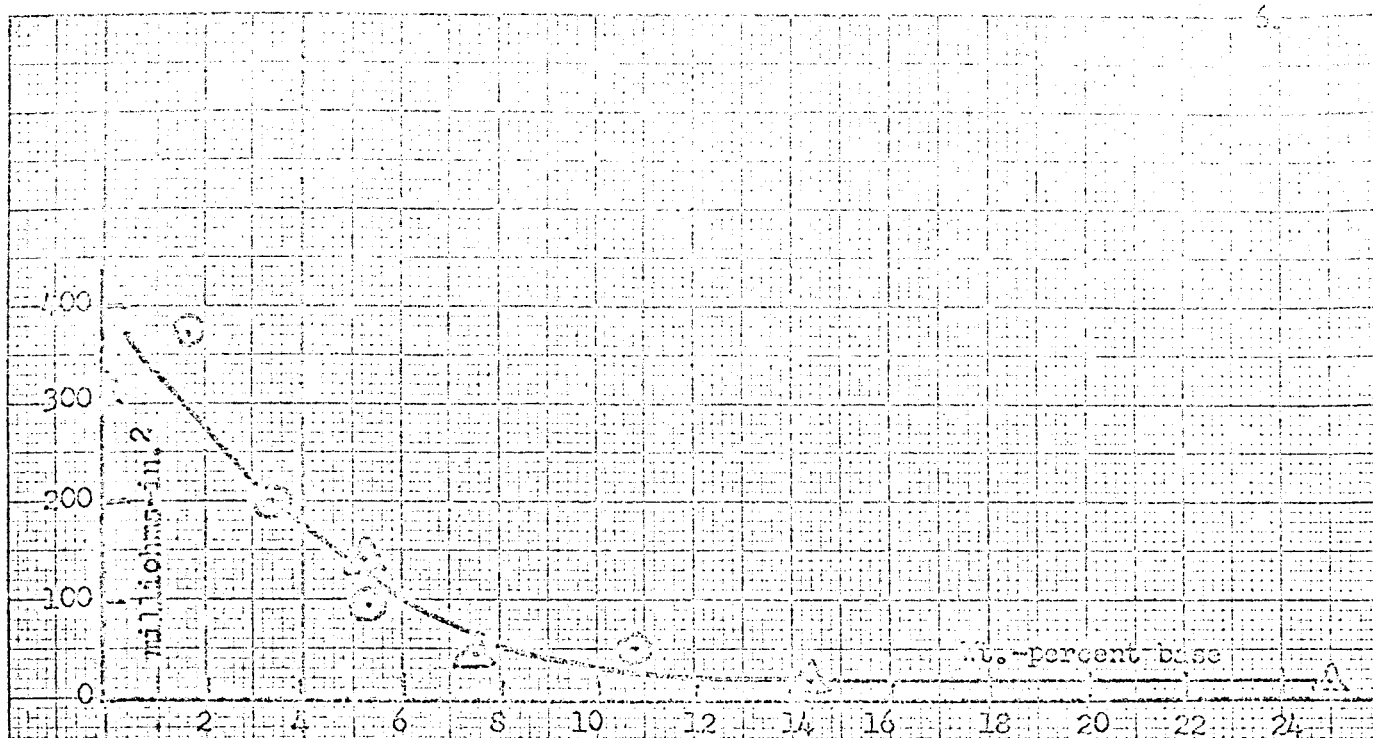


Fig. 1. Effect of Base on Resistance of B3,3 Film

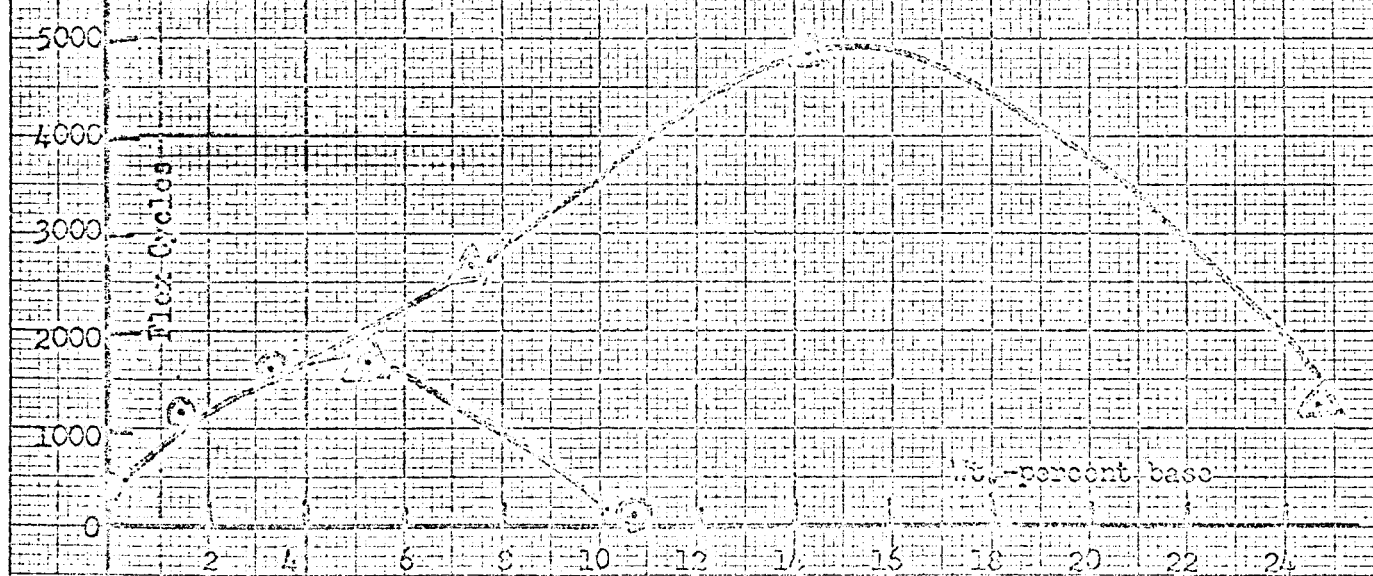


Fig. 2. Effect of Base on Flex of B3,3 Film

⊙ = Potassium Hydroxide

△ = 3-Hydroxypropylamine

Also included in Table I are the results of flex tests, which show that up to pH 4, KOH and hydroxypropylamine flexibilize to a small and equal degree. When higher amounts of the bases are added, the amine flexibilizes more than KOH. This is also shown in Figure 2 in which flex is plotted against weight-percent of base. With proportions above six weight-percent, and up to about 15%, it is more advantageous to use hydroxypropylamine instead of KOH even though both bases result in the same low electrolytic resistance: in this concentration range KOH tends to embrittle the film whereas hydroxypropylamine, to the contrary, flexibilizes quite efficiently.

Experiments in which triethanolamine (TEA) was added at increasing levels to B2 and C2 formulations are summarized in Table II. Formulation B2 is 20% polyacrylic acid plus 80% methyl cellulose. Formulation C2 is 20% 1:1 copolymer of vinyl methyl ether and maleic anhydride, 80% methyl cellulose. Figures 3 and 4 correspond to the experiments with B2 and C2 respectively. The resistance decreases with increasing TEA in both cases. Substantial increases in flexibility were effected at amine levels above about six percent.

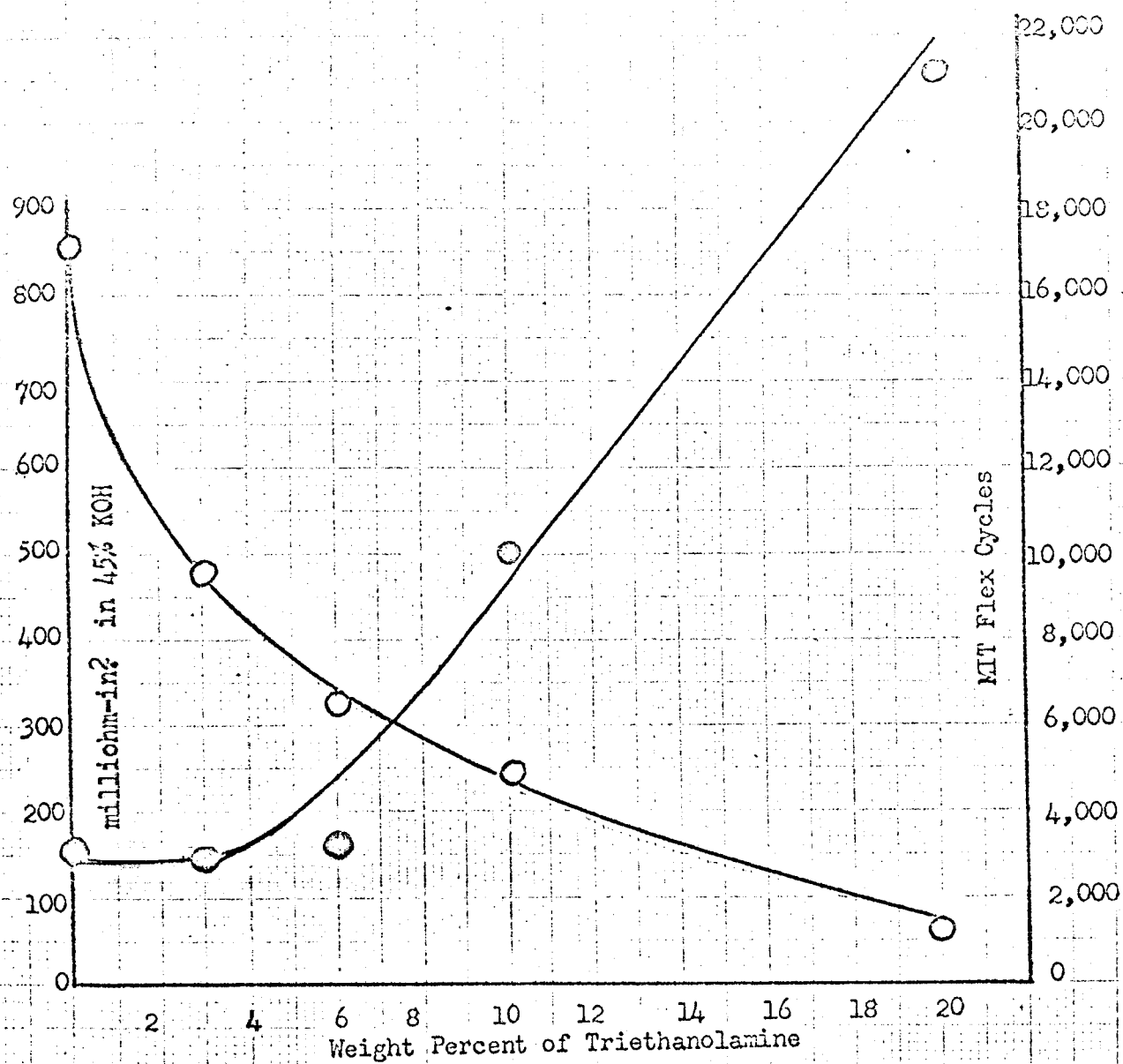


Fig. 3. Effect of Triethanolamine on Flex (○) and Resistance (○) of B2 Films

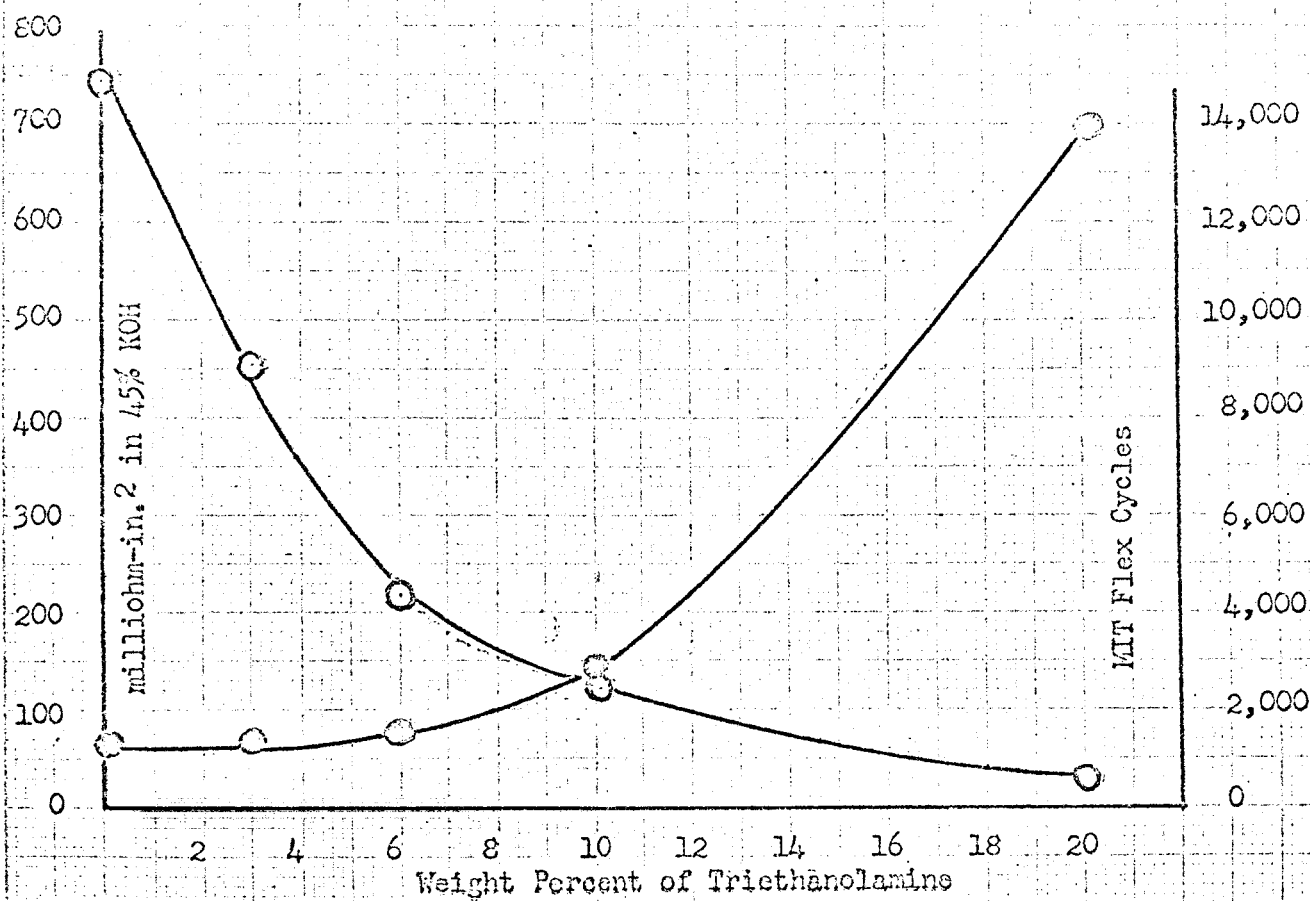


Fig. 4. Effect of Triethanolamine on Flex (○) and Resistance (○) of C2 Films

TABLE II. - Films Modified with Triethanolamine

Reference	Polymer Formulation (a)	TEA % on Polymers	pH (b)	Resist- ance in 45% KOH milli- ohms-in. ²	Physical Properties - 72° F. - 50% RH			
					MIT Flex (c)		Tensile Strength (d)	
					mils	cycles	psi	Elong., %
522-22	B2	0	2.6	848	1.5	3,001	10,830	25
522-27	B2	3	3.9	477	1.3	2,815	10,700	6
522-28	B2	6	4.1	327	1.4	3,181	9,070	18
522-29	B2	10	4.5	245	1.3	9,850	7,000	20
522-30	B2	20	5.3	60	1.4	21,000	5,220	26
522-24	C2	0	2.8	738	1.5	1,239	12,600	8
522-31	C2	3	3.6	448	1.9	1,324	11,300	5
522-32	C2	6	3.8	216	1.4	1,623	10,070	6
522-33	C2	10	4.1	122	1.3	2,838	7,470	22
522-34	C2	20	5.7	29.1	1.4	13,850	4,870	27

(a) B2 is 20 parts by weight polyacrylic acid plus 80 parts methyl cellulose.

C2 is 20 parts by weight poly(vinyl methyl ether-maleic anhydride 1:1) and 80 parts methyl cellulose.

(b) pH of a 10% aqueous solution of polymer mixture after addition of stated amount of triethanolamine.

(c) ASTM Test D643-43, at 200 g. tension.

(d) 1 inch span 2 inches per minute.

Extractability of Amine:

Under the conditions used for testing film conductivity, hydroxypropylamine (HPA) and triethanolamine are essentially completely removed from the methyl cellulose-polyacid films while they are being equilibrated in a large excess of agitated electrolyte solution prior to being introduced into the conductivity cell. After equilibration, blotted films have shown zero nitrogen content by Kjeldahl analysis. Complete extraction has also been demonstrated under conditions of no agitation in a Petri dish with electrolyte/film ratio equal to 25.

The question arises as to how close these conditions of complete extractability correspond to the conditions of the battery cell. With this in mind, an experiment was made with initial ratio of electrolyte to film equal to 6.3. This was accomplished by using two polyethylene forms having the dimensions of electrodes. The forms were U-wrapped with five turns of C2A film (C2 containing 10% HPA on polymer), packed tightly with polyethylene shims into a battery cell and covered with 30% KOH. After three days, the wrapped electrolyte forms were removed and unwrapped. The blotted film was submitted to Kjeldahl analysis for nitrogen. An unsoaked film of the same dimension was analyzed by the same method. The results indicated that only about 35% of the amine was extracted by the electrolyte. In commercial cells having lower electrolyte/film ratio, extraction might be still lower.

Depending on the degree of emphasis this type of film receives in future testing, further study should be made of the kinetics and equilibrium involved in the partition of extractable amines between membrane and electrolyte liquid.

B. Modification of Methyl Cellulose Films with Salts of Organic Acids

The use of organic salts to modify the properties of methyl cellulose was initiated under the previous contract. Investigation has been extended to cover the aliphatic series from formate to hexanoate and to include a number of dibasic salts. New results are summarized in Table III. The dependency of electrolytic resistance on the salt equivalents per methyl cellulose monomer unit is illustrated in Figure 5. It is evident that the lower members of the homologous series show a downward trend in resistance as the salt equivalent is increased. Within the precision limits of these experiments the dibasic salts follow pretty much the same trend as the monobasic salts, although the dibasic salts appear on the graph to be just a little bit more effective. Salts of the higher members of the aliphatic series beginning with valerate are poor in lowering resistance.

Table III. - Modification of Methyl Cellulose with Potassium Salts
of Organic Acids

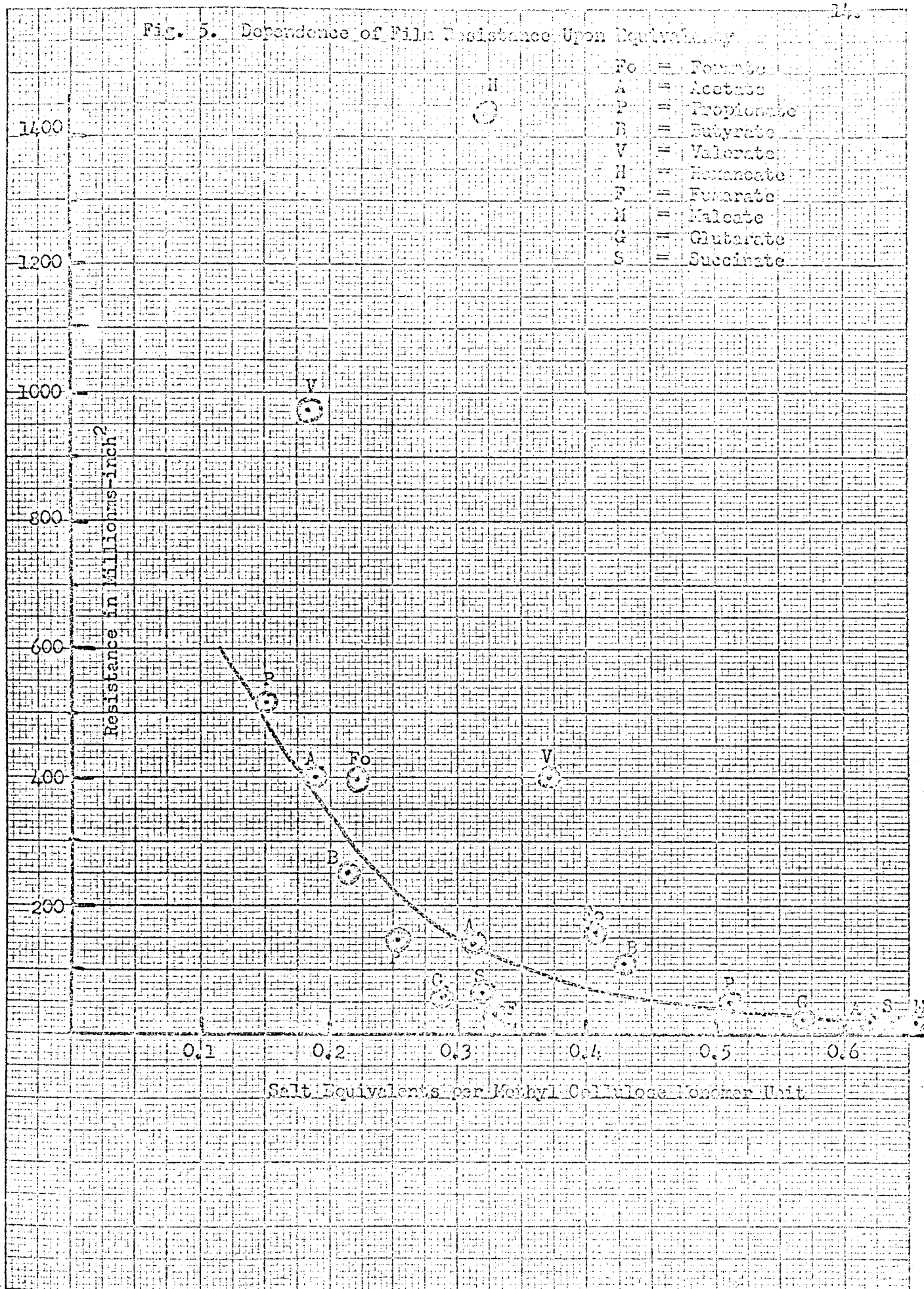
Reference	Potassium Salt Added	Weight % on MC	Equiv./ Equiv.MC	Elec.Res. 45% KOH milli- ohms-in.2	Film Thick- ness mils	MT Flex Cycles	Tensile Elong. psi %
<u>Monobasic Acids</u>							
449-145	None	0	0	7250	1.50	5,355	
534-56	Propionate	9.1	.152	515 (A)	1.45	5,234	8,040 47
-57	"	15.2	.254	147 (A)	1.8	5,015	6,290 51
-58	"	30.2	.510	50 (A)	1.9	12,230	3,500 57
534-91	Butyrate	14.3	.214	226 (A)	1.4	5,154	- -
482-121	"	28.6	.428	110 (A)	1.4	7,591	- -
534-130	Valerate	13.7	.184	971	1.4	4,190	5,640 47
534-129	" (F)	27.4	.372	400	1.5	6,917	6,790 32
534-132	Hexanoate	13.3	.162	2444	1.5	3,998	7,880 39
534-131	"	26.6	.324	1435	1.6	4,530	5,640 47
<u>Dibasic Acids</u>							
534-126	Glutarate	16.4	.29	57	1.5	3,154	6,260 45
-125	" (F)	32.9	.57	21	1.6	2,735	3,830 36
534-128	Succinate	15.8	.32	66	1.5	3,467	6,620 43
-127	" (F)	31.6	.64	20	1.6	1,508	4,000 34
482-140	Fumarate (F)	16.3	.33	32.9	1.8	3,514	6,760 40
-139	" (F)	32.6	.66	12.0	1.5	1,724	6,100 20
482-142	Maleate	16.3	.33	25.6	1.5	3,656	6,750 38
-141	"	32.6	.66	14.8	1.65	648	4,280 26

(A) Measurements in Shair cell, with less sensitive equipment than Kelley Salkind Cell now used.

(F) Frosted out on standing.

Fig. 5. Dependence of Film Resistance Upon Equivalency

14.



C. Modification of Methyl Cellulose By Pre-Swelling in 15% KOH

As disclosed on p. 11 of the Final Report NAS 5-9107 the electrolytic resistance in 45% KOH of a methyl cellulose film was markedly lowered by pre-swelling in 15% KOH.

An improvement of similar order was found when the film, after pre-swelling in 15%, was equilibrated by three days stirring in a large excess of 30% KOH, as shown below:

	Pre-Swollen in 15% KOH then Equilibrat- ed in 30%	Directly in 30% KOH
Swollen wt./orig.wt.	1.25	1.485
Resistance in 30% KOH milliohms-in. ²	17.3	498
Silver diffusion rate, in arbitrary transfer units to be defined in the Second Quarterly Report.	8.2	0.24

As can be seen, the film was opened up not only to hydroxyl ions but to silver ions as well. This will be discussed more fully in the Third Quarterly Report.

D. Modification of Methyl Cellulose and Methyl Cellulose/Polyacids
With Glycols and Related Materials

Several glycols were found to be compatible with methyl cellulose and methyl cellulose-polyacid solutions. Compatible mixtures containing these and related hydroxylated additives were cast to evaluate film properties. As seen in Table IV resistance was lowered in some instances, but not as effectively as in the case of amines.

Ethylene glycol, diethylene glycol, tetraethylene glycol and methyl cellosolve were all found to be completely miscible with 30% and 45% KOH so that it is possible to invoke extractability by the electrolyte as a factor in the lowered resistance. Weight changes of the films in 45% KOH were as shown below:

	<u>Ratio of Swollen Weight to Original Weight</u>
MC 15	1.25
MC + 20% diethylene glycol	1.26
C2	1.52
C2 + 20% diethylene glycol	1.54

TABLE IV. - Effect of Glycols and Related Additives on Properties of Methyl Cellulose Membranes

Reference	Base Polymers	Additive	On Polymers %	Resist- ance 45% KOH milli- ohms-in. ²	MIT Flex 50% R.H.	
					Mils	Cycles
458-118	MC15	None	-	6,080	1.5	3537
522-114	MC15	Ethylene glycol	20	3,610	1.4	6747
522-115	MC15	Diethylene glycol	20	566	1.6	4170
522-116	MC15	Tetraethylene glycol	20	2,110	1.6	4964
522-117	MC15	Carbowax 300	20	11,280	1.6	7446
522-118	MC15	Methyl Cellosolve	20	8,450	1.4	5972
522-123	C2	None	-	1,021	1.5	1846
522-130	C2	Diethylene glycol	10	236	1.6	1494
522-131	C2	" "	20	123	1.6	1143
522-134	C2 + KOH to pH 4	" "	10	151	1.3	2065
522-135	C2 + KOH to pH 4	" "	20	94	1.6	1326
522-133	B2 + KOH to pH 4	None	-	728	1.5	2957
522-136	B2 + KOH to pH 4	Diethylene glycol	10	590	1.6	2512
522-137	B2 + KOH to pH 4	" "	20	628	1.6	2139

E. Effect of Elevated Temperatures on C3 Film

While previously reported tests have shown that C3 film is resistant to degradation at 50° C. in the wet state, it appeared of interest to examine also its stability under the effect of dry heat.

The effect of exposure to dry heat of a C3 film was examined by U-wrapping the film around polyethylene forms simulating electrodes and heating at an average temperature of 57° C. for five hours. Just after its removal from the oven the dry film was so brittle that it was cracked by a single bend. On the other hand, when the assembly was re-equilibrated to the original condition (50% R.H.) employed in making flexural measurements the following values were obtained:

	<u>Cycles MIT Flex</u>
Original Film (499-15, 1.5 mil film)	754
Re-equilibrated at 50% R.H., 23° C.	
(Straight section)	701
(At bend)	632

It was concluded that under test conditions the chief effect was to remove the 9% moisture which is normally present to plasticize the film at 50% R.H. and that the effect is reversible.

F. Effect of Radiation on C3 Film

Two sealed silver-zinc cells (Yardney) with C3 as separators were received from NASA for examination. One had been irradiated with 1.18×10^7 rads from a Cobalt-60 source in an oven at temperatures from 40° to 55° C. The other was a control which had been in the same oven during the test but without irradiation. A corresponding two cells with cellophane separators instead of C3 were likewise used for radiation and control in the NASA test and returned to Yardney for examination. NASA reports that the layers of cellophane in the irradiated cell were very tightly "welded" together and tore when attempt was made to separate them, so that strength could not be determined.

Both polystyrene cell-case and potting of the irradiated cell were discolored to brown. The control cell appeared relatively unharmed. The cells were carefully opened with the aid of a fine saw. The electrolyte was removed from each cell and set aside in stoppered tubes for possible future analysis for organic carbon. The C3 membranes were unwrapped, cut into strips for tensile tests and stored in 30% KOH until tested.

The films from both cells were visibly silvered. Their thickness was less than the expected swollen thickness. The 436-134 lot of C3 film from which Yardney prepared the cells had average thickness 1.5 mils, which swells in 30% KOH to 2.2 mils. Yet the irradiated and control cells yielded material of thickness 1.6 and 1.4 respectively. It is not clear to what extent the discrepancy is attributable respectively to film erosion, or to reduced swelling in the geometrical confines of the shim-modified cell.

Tensile tests are recorded in Table V. Inspection shows that elongation is significantly reduced by the irradiation to 4% instead of 26% for the control. Average tensile strength was reduced by irradiation from 1.59×10^3 psi to 1.22×10^3 psi ($\pm 0.20 \times 10^3$ psi, pooled standard deviation). Statistical analysis of variance, by F-test, indicates less than 3% chance that this difference could be due to random variation.

TABLE V. - Effect of Irradiation on Tensile Properties
of C3 Film

Wrap No. from Ag Electrode	Control (#19 Cell)				Irradiated (#7 Cell)			
	Thickness Avg. mils	Lbs. to Break	Tensile psi	Elong. at Break %	Thickness Avg. mils	Lbs. to Break	Tensile psi	Elong. at Break %
5	1.60	1.615	1637	32	1.43	1.315	1557	7
4	"	1.613	1703	33	"	.817	966	3
3	"	1.603	1697	32	"	1.078	1277	3
2	"	1.493	1493	15	"	1.075	1067	3
1	"	1.346	1430	19	"	Too weak to test		
Avg.	1.60	1.534	1592	26	1.43	1.071	1217	4

G. Gas Evolution in C3 Cells

NASA has communicated privately that frothing has been observed during the charging of Burgess cells made with C3 separator. Electrical equipment and cells were loaned to CRL to permit observation of the behavior of the cells during charging. A battery of three cells was charged at 500 milliamperes for 24 hours. One of the cells was connected by capillary to a water-filled U tube and the evolved gas collected during the first nine hours of charge. Foam was not sufficient to escape as such out of the cell. From the fourth to ninth hour 7 ml of gas was evolved. KOH and pyrogallol were dissolved under nitrogen in the water leg opposite the gas and the thus prepared oxygen-absorbing solution was magnetically stirred. There was no shrinkage in volume or discoloration of the pyrogallol. The evolved gas, therefore, could be neither CO₂ nor oxygen, a logical suspect. An attempt to ignite the gas was unsuccessful. Its identity as hydrogen is, nevertheless, suspected. It is unlikely that the gas could be a decomposition product of C3.

It seemed possible that a significant dilution of the electrolyte by the acid of C3 could contribute to frothing by dissolving cellulosic material of surface active properties. The degree of this dilution was calculated by careful weighing of the separator of an unfilled cell and the 30% electrolyte added to just cover the electrode assembly. The weights were respectively 10.0353 grams C3 film and 36.2 g. 30% KOH. From the acid content of PVMA (30%) it was calculated that the average concentration of electrolyte at equilibrium would be reduced to 24.8%. The concentration within the film could be lower, depending on the exchange rate.

An obvious way of combating this dilution would be to pre-neutralize the PVMA in the C3. Attempts to do this have been accompanied by marked changes in the character of the film. Work in this area is continuing.

H. Shorting of Cells on Standing

Shorting and loss of ampere hour capacity of cells employing C3 membranes on standing three months or less in the charged condition has been observed in silver-zinc cells at NASA and in silver-cadmium cells by the Jet Propulsion Laboratory. The latter reported that the membrane was extensively silvered. One such self-discharged cell was disassembled for examination. The physical strength of the C3 wrap appeared to be good and no cracks in the wrap were noted. It was black of uniform shade from the first wrap around the electrode to the sixth wrap.

The second and fifth wraps were cut out, digested in concentrated nitric acid and silver content determined by potentiometric titration with KI. Results confirmed the visual observation that silver was distributed rather uniformly throughout the separator.

For comparison a silver-zinc cell from NASA which had undergone over 80 cycles but had not been subjected to long stand times was disassembled and examined. Unlike the above the wraps close to the electrode were heavily silvered, with the silver usually decreasing in amount from the first to the sixth wrap where much of the surface was still transparent, showing silver only in spots. The first and fifth wraps of the separator were digested and analyzed for silver in the same way. Comparison is given in Table VI.

TABLE VI. - Distribution of Silver on Separator Wraps

	mg. Ag/sq. in.		
	1st Wrap	2nd Wrap	5th Wrap
Ag/Cd Cell - after 3 months stand time	-	8.45	7.82
Ag/Zn Cell - after 85 cycles	31.2	-	1.4

Results indicated that under the stand time condition silver migrates through the C3 developing to a "soft short", which leads to discharge. Under conditions of charge and discharge, however, the separator appears to operate satisfactorily in that each wrap performs in a serial removal of the silver.

Work in this area is continuing here and at NASA.

J. Physical Modification of Polyethylene Films

Inasmuch as the addition of KOH-extractable substances to methyl cellulose results in reduced electrolytic resistance, the possibility suggested itself that an analogous treatment of polyethylene might have similar results.

Two types of polyethylene film were investigated, a packaging film and an ionomer, Surlyn A 1601. These were chosen on the basis of compatibility and swellability by phosphorus trichloride, the additive principally studied. The packaging polyethylene was soluble in warm PCl_3 . At room temperature it softened with no measurable increase in thickness. The Surlyn film was measurably swollen at room temperature.

After the soaking operation the films were given various after-treatments to remove the solvent, as indicated in Table VII. It is evident that drastic changes in resistance are indeed possible by this experimental approach, the resistances in some cases are reduced to one-hundredth or one-thousandth of the original resistance. However, the resistances are still too high for the films to be of practical interest. Further modifications of this approach may be more fruitful.

TABLE VII. - Effect of Swelling in Solvent Followed by Extraction
in 45% KOH Upon Resistance of Polyethylene-Type Films

Reference	Polymer	Solvent	Solvent-Treatment	After-Treatment	Resistance 45% KOH milli- ohms-in. ²
483- 136	PE*	none	none	Control	1.6×10^6
138	PE*	PCl ₃	6 hrs. 25° C.	10 days soak in 45% KOH	1.1×10^4
140-1	PE*	PCl ₃	16 hrs. 36° C.	7 days soak in 45% KOH	7.8×10^4
140-2	PE*	PCl ₃	3 days 36° C.	3 days soak in 45% KOH	1.7×10^5
145	Surlyn A1601**	none	none	Control	3.1×10^6
145-1	Surlyn A1601	PCl ₃	2 hrs. 25° C.	3 days stir in 45% KOH	6.2×10^4
146-1	"	PCl ₃	24 hrs. 25° C.	7 days stir in 45% KOH	2.9×10^3
144	"	PCl ₃	4 hrs. 43° C.	-	dissolved
146-2	"	PCl ₃	4 hrs. 32° C.	-	disintegrated
522- 127-1	"	PCl ₃	3 days 25° C.	ice water, 45% KOH 24 hrs.	3.1×10^4
127-2	"	PCl ₃	3 days 25° C.	ice water, 45% KOH 24 hrs.	4.2×10^4
483- 147-1	"	toluene	dioxane, water	KOH 3 days	3.8×10^5
147-5	"	Dioxane	75 min. 50° C.	KOH 3 days	1.2×10^5
	PUDO Cellophane		-	-	1.1×10

* "Baggie", Colgate-Palmolive

** Boyertown Packaging Service - Acrylic ionomer

K. Polyvinyl Pyridine-Polyacid Co-acervate Films

Experiment showed that aqueous solutions of polyvinyl pyridine hydrochloride and polyacrylic acid may be mixed to form a clear homogeneous solution. This is in contrast to what happens when alcoholic solutions of polyvinyl pyridine and polyacrylic acid are mixed: in that case the strong attraction between the basic and acidic polymers resulted in immediate precipitation of a coacervate. Clear homogeneous films were prepared from the aqueous solution by casting on glass and drying until chloride-free. The dry films are so brittle that direct removal from the glass is extremely difficult. However, if the films are first soaked in concentrated KOH they may be easily removed from the glass.

Proprietary preparations of both 4-vinyl and 2-vinyl pyridine suspension polymers were studied. The 1:1 copolymer of vinyl methyl ether and maleic anhydride may be used instead of polyacrylic acid. Resistance measurements and other properties are summarized in Table VIII.

The rate of silver diffusion was close to that of films made from C3 and related methyl cellulose compositions. The vulnerability to oxidation by silver oxide during the diffusion test was the lowest of all films tested. Further reference to this property will be made in the Second Quarterly Report under this contract.

Practical exploitation of this co-acervate approach would necessitate research effort to improve flexibility and release properties without impairing of the desirable electrical performance and stability.

TABLE VIII. - Properties of Polyvinyl Pyridine-Polyacid
Co-Acervate Films

Sample No.	482- 127	574- 99	574- 110	574- 97
<u>Composition</u>				
Poly 4-vinyl pyridine	1.00	1.00	1.00	-
Poly 2-vinyl pyridine	-	-	-	1.00
Polyacrylic Acid (Acrysol A5)	1.00	0.75	-	1.00
PVMA	-	-	1.00	-
<u>Resistance in ohms-cms.</u>				
30% KOH	8.7	16.0	8.2	15.0
45% KOH	280	490	154	409
<u>Resistance after heating 33 days at 50° C. in electrolyte solution (ohm-cms)</u>				
30% KOH	6.7	-	-	-
45% KOH	154	-	-	-
MIT Flex at 50% R.H., cycles	90	-	-	-
Tensile Strength at 50% R.H., psi	2950	-	-	-
Elongation at break, per cent	6	-	-	-
Silver diffusion av. rate % orig. Ag per day	13.2	-	-	-
Silver reduced on film, % orig. Ag per day	0.14	-	-	-

ITEMS OF NEW TECHNOLOGY

I. METHYL CELLULOSE-POLYACID FILMS MODIFIED WITH AMINES

Methyl cellulose-polyacid films may be prepared with extremely low resistances in 45% KOH by casting them from solutions buffered to pH in the range 3 to 6. At pH above 4 hydroxyamines like 3-hydroxypropylamine and triethanolamine are more effective than potassium hydroxide in that they act as flexibilizing agents for the dry film, making for superior facility in handling.

Addition of 10% triethanolamine to B2 Formulation (20% polyacrylic acid; 80% methyl cellulose) lowers resistance by 70%, increases flexibility by 330%. Addition of 10% triethanolamine to C2 Formulation (20% 1:1 copolymer of vinyl methyl ether and maleic anhydride; 80% maleic anhydride) lowers resistance by 83%, increases flexibility by 230%.

Both hydroxypropylamine and triethanolamine are completely soluble in 45% KOH and have been shown to be extractable under conditions of the resistance test. The extractability is believed to be a factor in the lowered resistance.

II. METHYL CELLULOSE FILMS MODIFIED WITH SALTS OF ORGANIC ACIDS

In extending the study of this type of system to include higher aliphatic acids and lower dibasic acids, resistance lowering was found to be related to the acid equivalents added per methyl cellulose monomer unit.

III. METHYL CELLULOSE FILMS MODIFIED BY PRESWELLING IN DILUTE POTASSIUM HYDROXIDE

A methyl cellulose film, equilibrated first in 15% KOH, then in 30% KOH, gave a resistance of 17.3 milliohms-in.² on a 1.5 mil film as against 798 milliohms-in.² when equilibrated directly in 30% KOH. Accompanying the resistance lowering, a thirty-fold increase in the diffusion rate of silver occurred.

ITEMS OF NEW TECHNOLOGY (CONTINUED)IV. METHYL CELLULOSE-POLYACID FILMS MODIFIED WITH GLYCOLS

Ethylene glycol, diethylene glycol, tetraethylene glycol, and methyl cellosolve are all compatible with methyl cellulose and methyl cellulose-polyacid solutions and good films may be cast from these solutions. However, the glycols are not as effective as certain amines (like HPA or TEA) in lowering the electrolytic resistance of the films in KOH.

V. RESISTANCE OF METHYL CELLULOSE-POLYACID SEPARATOR TO IRRADIATION

A C3 separator recovered from a silver-zinc cell irradiated by Cobalt 60 had lost only 24% of its wet tensile strength. Composition of C3 is 30% 1:1 copolymer of vinyl methyl ether and maleic anhydride; 70% methyl cellulose. NASA reports that cellophane separators under same exposure became welded together.

VI. POLYVINYL PYRIDINE-POLYACID CO-ACERVATE FILMS

A co-acervate of poly(4-vinyl pyridine) and polyacrylic acid may be prepared as a clear film by mixing aqueous solutions of the polyacid and of the hydrochloride of the polyvinyl pyridine, casting the aqueous solution on glass and drying until chloride free. The dried film is extremely brittle but may be handled as a swollen film after soaking in concentrated potassium hydroxide. The swollen film has relatively low resistance to electrolytic current, fair retardation of silver ion diffusion and very low vulnerability to chemical oxidation by silver oxide.

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E r r a t a

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First Quarterly Report

Contract NAS-5-9107, Modification 6

Kindly replace Figures 3 and 4 by the corrected copies herewith submitted.

Also make the following corrections:

On page 2, paragraph 2, line 4

Also

On page 27, paragraph 2, line 4

The composition of C2 has 80% methyl cellulose

(not maleic anhydride)